Refinement of the ruby luminescence pressure scale

Wilfried B. Holzapfel
Universität Paderborn, Department Physik, D-33095 Paderborn, Germany

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A comparison of recent high pressure x-ray diffraction data for diamond and Ta with low pressure ultrasonic data provides a basis for the refinement of the ruby luminescence pressure scale, whereby not only the slope and curvature parameters \( A = 1904 \) GPa and \( B = 7.665 \) of the previous scale are changed, but evidence is given for a modified form for the ruby \( R_1 \) luminescence line shift under pressure with \( A = 1820 \) GPa, \( B = 14 \), and an additional parameter \( C = 7.3 \). This revised ruby pressure scale resolves to a large extent previous discrepancies between equation of state data derived from x-ray measurements on the basis of the currently used ruby scale, on the one hand, and ultrasonic or theoretical studies, on the other hand. © 2003 American Institute of Physics.

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INTRODUCTION

The development of the diamond anvil cell (DAC) for the generation of static pressures up to several hundred GPa was intimately related to the use of the ruby \( R_1 \) luminescence line shift for pressure measurements.\(^1\)\(^-\)\(^3\) Although the precision of this technique can give a resolution of \( \pm 10 \) MPa under hydrostatic conditions at room temperature,\(^4\) the (absolute) accuracy is expected to be only 1% near ambient conditions and 3% at 55 GPa as recently determined by an absolute calibration of the ruby scale based on combined x-ray and Brillouin scattering measurements on MgO up to this pressure.\(^5\) Due to the nonlinearity of the ruby \( R_1 \) line shift with pressure\(^6\) expressed by the parameter \( B \) in the form

\[
\lambda = \lambda_0 (1 + p \cdot B/A)^{1/B} \quad \text{or} \quad p = (A/B) \left[ \left( \lambda/\lambda_0 \right)^{B} - 1 \right],
\]

the present uncertainties in \( B \) result in much larger uncertainties at higher pressures. Nonhydrostatic conditions in most of the previous calibrations lead to additional uncertainties in the currently used ruby luminescence scale.\(^7\)\(^,\)\(^8\) Furthermore, one should notice that uncertainties in \( A \) and \( B \) are directly related to corresponding uncertainties in \( K_0 \) and \( K'_0 \), the isothermal bulk modulus and its isothermal pressure derivative near ambient conditions, when the ruby luminescence is used for pressure measurements in equation of state (EOS) studies with x-ray diffraction. The relative uncertainty in \( A \) gives direct similar systematic uncertainties in the values for \( K_0 \). The uncertainty in \( B \), however, involves the ratio \( K_0/A \) in error estimates of \( K'_0 \) by the form

\[
\Delta K'_0 = \Delta B \cdot K_0/A.
\]

For highly compressible materials like the heavier rare gas solids\(^9\) with \( K_0 \approx 3 \) GPa the corresponding uncertainty \( \Delta K'_0 \approx 0.005 \) is very small with respect to other uncertainties. However, for incompressible solids like diamond\(^10\) with \( K_0 = 441.8(1) \) GPa, one finds with \( \Delta B \approx 4 \) a \( \Delta K'_0 \approx 1 \), and this is just the order of magnitude for the discrepancy found between the ultrasonic value and the value from a recent single crystal x-ray diffraction study on diamond up to 140 GPa using He as a nearly hydrostatic pressure transmitting medium\(^11\) and ruby for the pressure determination on the basis of the “quasihydrostatic” pressure scale.\(^7\) The results of this very precise study on diamond\(^11\) are compared in Table I with ultrasonic,\(^9\) theoretical,\(^12\),\(^13\) and shock wave results,\(^14\) respectively. The discrepancy seen there in the average value \( K'_0 = 4.0(5) \) from ultrasonic and theoretical data, on the one hand, and the much smaller values from the shock wave and x-ray measurements, on the other hand, gave the initial hint for the necessity to revise the ruby scale and to get more realistic estimates for the uncertainties, which should be taken into account in future estimates of absolute uncertainties in \( K_0 \) and \( K'_0 \) values derived from x-ray diffraction measurements in DACs using the ruby \( R_1 \) line shift for the pressure measurements. Similar discrepancies were noticed more recently\(^15\) in a high pressure x-ray study on Ta, and unusual data\(^16\) for Os finally stimulated the present study with its ambition to resolve this dilemma.

According to International Union of Pure and Applied Physicists (IUPAP) standards the estimated uncertainties of the last digit for any given numerical value are added in round brackets as shown above for the values for \( K_0 \) and \( K'_0 \).

DATA ANALYSIS

A critical inspection of the previous calibrations of the nonlinear ruby line shift under pressure in the 100 GPa range\(^5\)\(^-\)\(^8\),\(^17\) indicates that these calibrations were based exclusively on EOS data derived from shock wave measurements. Since the evaluation of \( K_0 \) and \( K'_0 \) values from shock wave data involves an extrapolation down to low pressures, one can expect that these extrapolated values have larger errors than directly measured ultrasonic data. For Cu, Ag, and Au, a detailed comparison of these differences recently showed\(^18\) that the original shock wave data themselves are indeed compatible with the ultrasonic data and only the “extrapolated” \( K_0 \) and \( K'_0 \) values from the shock wave studies deviate from the ultrasonic values. This observation is illustrated in more
TABLE I. Values for the (isothermal) bulk modulus \( K_0 \) and its (isothermal) pressure derivative \( K'_0 \) for diamond at ambient conditions derived from ultrasonic, theoretical, dynamic shock wave, and static x-ray diffraction studies (using the “quasihydrostatic” MX86Ruby scale with \( A = 1904 \text{ GPa} \) and \( B = 7.665 \)). The theoretical value of \( K_0 = 442(1) \text{ GPa} \) for a lattice parameter of \( a = 355 \text{ pm} \) for zero pressure (Ref. 12) has been rescaled here to obtain \( K_0 \) for the experimental value of \( a_0 = 356.7 \text{ pm} \) by the relation \( K_0 = K - (a/a_0)^3 K'_0 \) using \( K'_0 = 4 \).

<table>
<thead>
<tr>
<th>Technique</th>
<th>( K_0 ) (GPa)</th>
<th>( K'_0 )</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ultrasonic</td>
<td>441.8(1)</td>
<td>4.0(7)</td>
<td>11</td>
</tr>
<tr>
<td>theory</td>
<td>417(5)</td>
<td>4.1(4)</td>
<td>12</td>
</tr>
<tr>
<td>shock waves</td>
<td>519</td>
<td>2.6</td>
<td>13</td>
</tr>
<tr>
<td>static XRD with</td>
<td>444(3)</td>
<td>2.5</td>
<td>14</td>
</tr>
<tr>
<td>MX86Ruby-scale</td>
<td>447(7)</td>
<td>3</td>
<td>11</td>
</tr>
</tbody>
</table>

In detail Fig. 1, which shows for just a few cases, that one can notice a strong correlation in the deviations of \( K_0 \) and \( K'_0 \) values derived from ultrasonic measurements with respect to the data from shock wave studies. It goes too far to discuss this longstanding discrepancy between ultrasonic and (extrapolated) shock wave data here in detail, but one should notice in Fig. 1 that there are indeed some materials, like W, for which the discrepancies are very small, and these materials should be considered as especially favorable for calibrations of the ruby line shift.

In a detailed analysis of the possible uncertainties in the present ruby scale, one must notice that the value for \( A = 1904 \text{ GPa} \) in Eq. (1) in both the “nonhydrostatic” MB78Ruby-scale and as in the “quasihydrostatic” MX86Ruby scale was quoted as the “initial slope form Piermarini et al. (1975).” However, the original values of the “linear” PB75Ruby-scale, \( dP/d\lambda = 2.73(3) \text{ GPa/nm} \) for the range from 0 to 10.4 GPa and 2.753(12) GPa/nm for the range from 10.4 to 19.5 GPa, can be considered only as effective values for average pressures of 5 and 15 GPa, respectively. For the nonlinear MX86Ruby-scale with \( B = 7.665 \) for “quasihydrostatic” conditions, one obtains with this curvature the first two values for \( A \) in Table II. Later, it will be shown that more reasonable values for \( B \) may be as large as \( B = 15 \). With this stronger curvature even much smaller values for \( A \) would result from the PB75Ruby-scale as illustrated in Fig. 2 by the different values for \( \Delta p/p \) at ambient pressure for the scales discussed later, whereby one should notice that these values of \( \Delta p/p \) are equal to \( \Delta A/A \).

In fact a recent study at pressure below 1 GPa also resulted in a smaller value for \( A \) than previously accepted, although the accuracy in this study was rather limited due to correlations with thermal shifts as indicated by the corresponding error given with the data in Table II. Similarly, the first measurement of the ruby \( R_1 \) line shift at very low pressures (below 0.1 GPa) had given a rather small value for \( A \approx 1600 \text{ GPa} \), however, with a very large uncertainty, which cannot be estimated easily.

Furthermore, the recent “nearly hydrostatic” high-pressure x-ray diffraction studies on diamond and tantalum resulted in very precise \( K_0 \) values on the basis of the MX86Ruby-scale. Since these values for \( K_0 \) are directly proportional to the value of \( A \) in the MX86Ruby-scale, a comparison with corresponding \( K_0 \) values from ultrasonic measurements supports the suspicion that the value for \( A \) should be smaller indeed as indicated in Table II.

All these data together suggest that the value for \( A \) may be \( 5(3)\% \) smaller than the previously used value. Due to the correlation of the value for \( A \) with the value of \( B \) in any calibration performed over a finite range in pressure,

<table>
<thead>
<tr>
<th>Reference</th>
<th>( A ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref. 11</td>
<td>1871(30)</td>
</tr>
<tr>
<td>Ref. 11</td>
<td>1814(50)</td>
</tr>
<tr>
<td>Ref. 11</td>
<td>1875(30)</td>
</tr>
<tr>
<td>Ref. 19</td>
<td>1880(40)</td>
</tr>
<tr>
<td>Ref. 11</td>
<td>1788(20)</td>
</tr>
<tr>
<td>Ref. 20</td>
<td>1820(30)</td>
</tr>
</tbody>
</table>

TABLE II. Estimates of initial slopes \( A \) for the ruby \( R_1 \) line shift from different experimental data.

FIG. 1. Correlations of the differences \( \Delta K_0/K_0 \) and \( \Delta K'_0/K'_0 \) in the values from shock wave (Refs. 13, 21–24) and ultrasonic (Refs. 10, 25–32) studies for W, Cu, Ag, Au, ruby, and diamond.

FIG. 2. Pressure differences with respect to the MX86Ruby-scale in the “quasihydrostatic” x-ray diffraction experiment on W (open circles) (Ref. 8) and on diamond (Ref. 11), whereby the later data are obtained with an ultrasonic EOS using \( K_0 = 4.0 \) (open diamonds) and \( K'_0 = 3.5 \) (closed diamonds), respectively. Similarly the curve labeled Ta represents x-ray diffraction results (Ref. 15) on the basis of the MX86Ruby-scale, rescaled by the use of the best values for \( K_0 \) and \( K'_0 \) discussed in Table II. The open circle and the solid dashed lines represent the best value and the uncertainty of the absolute calibration (Ref. 5). Equation (3) is represented by the solid curve labeled HP02. The other curves with different values for \( A, B, \) and \( C \) illustrate the uncertainty of the present refinement.
one finds from the most recent calibration\textsuperscript{5} up to \( p_m = 55 \text{ GPa} \) with an estimated decrease of \( A \) by 84(30) \text{ GPa}, an increase of \( \Delta B = -2 \cdot \Delta A/p_m \approx 3(1) \) with respect to the value of \( B = 7.715 \) given there.

Especially the small value of \( K_0' = 3 \) from the recent x-ray diffraction study on diamond\textsuperscript{13} more closely. Figure 1 illustrates the anticorrelation between the shock wave and ultrasonic values for \( K_0 \) and \( K_0' \), not only for the previously analyzed data\textsuperscript{22} of Cu, Ag, and Au, but also for data\textsuperscript{2,29,32} of W, for the data\textsuperscript{10,13} of diamond, and for some data of ruby (Al\(_2\)O\(_3\)) from ultrasonic\textsuperscript{27} and shock wave measurements.\textsuperscript{21} The correlation of these differences for Cu, Ag, Au, and W is illustrated in Fig. 1 by the straight line, which indicates that the shock wave data suggest even a value of \( K_0' = 4 \) for diamond. Since the MX86Ruby-scale was calibrated with respect to the shock wave data for Cu and Ag, the deviations given by this correlation also apply directly to this ruby scale. Since the \( K_0' \) values used in this calibration have been too small, one also expects that value \( B = 7.665 \) given there must be too small. The “quasihydrostatic” conditions with Ar as a pressure-transmitting medium may have additionally affected the value of \( B \) in this case. Since W on the other hand is one of the few cases where the value for \( K_0 \) from ultrasonic measurements\textsuperscript{26,29} is very close to the shock wave data, as illustrated in Fig. 1 also, a later measurement\textsuperscript{8} with W and ruby to 110 GPa and with Ne as the pressure transmitting medium appears to be closer to a “nearly hydrostatic” case and more reliable with respect to the EOS data used in this measurement. This means that one should only compare these W data with calibrations on the basis of diamond EOS data. The best value of \( K_0' \) for diamond\textsuperscript{10,12,13} should be expected thereby to be around \( K_0' = 4.0(5) \). Similarly one can reanalyze the effect of the recent\textsuperscript{15} EOS data for Ta on the ruby scale. All these data must also be compared with the uncertainty of the absolute ruby calibration\textsuperscript{5} to 55 GPa to obtain a refined ruby scale compatible with all the existing data.

This comparison is illustrated in Fig. 2, whereby the “quasihydrostatic” MX86Ruby-scale with \( A = 1904 \text{ GPa} \) and \( B = 7.665 \) is taken as the reference line. The solid dashed lines thereby represent the uncertainty of the absolute calibration.\textsuperscript{5} This uncertainty was stated to be 1\% but it increases to 3\% at 55 GPa due to the uncertainties in the higher order polynomial coefficients of the elastic modules. At lower pressures the uncertainty also increases much above the 1\% value due to the limited accuracy of the x-ray diffraction technique. The differences in ruby line shifts are thereby converted to relative pressure differences \( \Delta p/p \) for a better visualization of the uncertainties at low pressures. The effect of different values for \( B \) in Eq. (1) is illustrated in Fig. 2 for constant \( A = 1904 \text{ GPa} \) by a set of almost straight lines, whereby the line for \( B = 5 \) corresponds to the MB78Ruby-scale and the line for \( B = 1 \) represents the original PB75Ruby-scale, which was calibrated only in the range from 0 to 20 GPa shown as a solid black line. The average value at 10 GPa indicates again that only smaller values for \( A \) corresponding to negative values of \( \Delta p/p \) at \( p = 0 \text{ GPa} \) agree with nonlinear ruby scales. Although a recent reevaluation of all the EOS data for NaCl proposes\textsuperscript{33} a larger value for \( K_0 \) and “correspondingly” a larger value for \( A \), this correction is taken into account here only by the size of the error bar but not as a shift, because the reevaluated value for \( K_0 \) does not fit the more accurate ultrasonic data.\textsuperscript{29}

The data for the ruby line shift from an EOS study on Ne (Ref. 8) using EOS data of W for cross-calibration are directly represented in Fig. 2 by the corresponding data points (solid dots), and these data probably represent the best nearly hydrostatic calibration on the basis of reliable shock wave and ultrasonic EOS data for W as illustrated already in Fig. 1.

A ruby calibration on the basis of EOS data for diamond can be obtained from the recent volume data\textsuperscript{11} by the use of the ultrasonic values\textsuperscript{10} for \( K_0 \) and \( K_0' \). The value \( K_0' = 4 \) thereby results in the relative pressure differences with respect to the MX86Ruby-scale shown by the open diamonds in Fig. 2. A fit of these data by Eq. 1 with \( A = 1904 \text{ GPa} \) results in \( B = 10.8 \) as indicated by the corresponding thin line, which deviates significantly from the W data at higher pressures. A value of \( K_0' = 3.7 \) for diamond, on the other hand, shifts the diamond data to the positions of the solid diamonds, which fit more reasonably into the region of the absolute calibration up to 55 GPa and also agree more closely with the W data at higher pressures. The remaining difference to the W data may be related to slight nonhydrostaticity in the surrounding Ne, which could shift these data to these slightly higher values. From this point of view \( K_0' = 3.7 \) seems to present for diamond the best compromise between the ultrasonic, theoretical, and static x-ray diffraction data and fits of Eq. (1) to these data result in the thin line corresponding to \( B = 9.9 \). Obviously these fits of the diamond data with Eq. (1) give strong hints for a different refinement to be applied to the ruby scale, because a different functional form with different slope not only at lower pressures but also at higher pressures would certainly improve these fits, independent of the precise value for \( K_0' \).

**THE HP02 FUNCTIONAL FORM**

Since Eq. (1) has some functional similarity to the Murnaghan EOS, which is known to be a good functional form only for moderate compressions,\textsuperscript{34–36} one may consider as a better form for the ruby line shift under strong compression the following relation:
used invertible EOS form, 37 and corresponds to Eq. which has some formal similarity to another less commonly calibration. 5

represent the best fix point from the “absolute” ruby the reference line at 30 GPa and this point is considered to notice that all these three fits pass through the solid dot on

K this form to these Ta data and to the diamond data with

thin dotted line may represent an upper limit for the limit of

C !~ represents the slope and curvature from Eq. with

400 GPa, where these thin dotted lines cross not only the middle dotted line

Fig. 2 remain rather close to the HP02Ruby-scale up to about the present form with a very different value for pressure, as illustrated in Fig. 3, where one can notice that

the present form with respect to relative volume \( V/V_0 \) of ruby. The data of the MX86Ruby-scale (solid dashed line) are compared with the present HP02Ruby-scale (solid line), with the simple power law Eq. (4) (dash-dotted line) and with the extended power series Eq. (5) representing the present best form for large changes in volume or density (dash-triple-dotted line). The inset presents an enlarged view of the small differences between the different forms with respect to the most regular simple power law [Eq. (4)] at moderate pressures.

A better insight into the remaining uncertainties of the HP02Ruby-scale can be obtained in more detail if one considers the physical background for the ruby luminescence line shift. Theoretical descriptions concerning the effect of pressure on the complete electronic structure of \( \text{Cr}^{3+} \) in ruby 38–41 only empirical scaling of the screening and effective charges are used so far but no first principal calculations. In fact, a total of three parameters for the screening and volume dependence of the effective charge and three parameters for the EOS of ruby (differing from the experimental EOS 42) were necessary to obtain a perfect fit 40 with the MX86Ruby-scale. Nevertheless these empirical models suggest that one should expect simpler volume dependences compared with the mathematically more complex pressure dependences. With the use of the (well known) EOS for ruby 42 the volume dependences of the wavelength \( \lambda \) or the wave number \( \nu \) for the ruby \( R_1 \) line can be derived with any of the previous forms for wide ranges in compression and the previous theoretical modeling suggests than a simpler functional form with respect to relative volume \( \nu = V/V_0 \), relative density \( \rho/\rho_0 \), or relative average interatomic distance \( r/V_0^{1/3} \). At this point one may notice that a positive value of \( C \) leads to a crossover (\( \nu = 0 \)) between the low spin \( 2E \) excited state and the high spin \( 4A_2 \) ground state of \( \text{Cr}^{3+} \) at a finite volume, or in other words to the expected spin quenching under (finite) pressure. An extrapolation of the MX86Ruby-scale, on the other hand, results in \( \nu = 0 \) only at infinite compression. With the use of a reasonable EOS for strong compression 34–36 the present HP02Ruby-scale at first shows a crossover with the MX86Ruby-scale at a relative volume \( \nu = V/V_0 \approx 0.6 \) before the quenching is approached around \( \nu \approx 0.4 \) or at a pressure in the range of 2 TPa. This stronger decrease of the transition energy as given by the present HP02Ruby-scale is illustrated in Fig. 4 together with some functional forms, which correspond to simpler volume dependences without the use of EOS data. Since any reasonable volume dependence should also represent a good inter-
polation between ambient conditions and the well-known free-ion-value\textsuperscript{33} for Cr\textsuperscript{3+} $v_s = 15\,056\,\text{cm}^{-1}$ or $v_s/v_0 = 1.0454$, the shift of the $R_1$ line is represented in Fig. 4 with respect to the relative density $\rho/\rho_0$ to show the approach to $v_s/v_0$ at $\rho/\rho_0 = 0$.

At first one may now try a simple power law with respect to the density $\rho$ or the relative interatomic distance $x$ of the form:

$$v = v_f - (v_f - v_0) x^{-q}.$$  

A fit of this form to the density dependent form of the present HP02Ruby-scale in Fig. 4 over the range from 0 to 150 GPa, where this scale was fitted against the diamond data, results in $q = 5.0$ and $v_f/v_0 = 1.085$ with a standard deviation of $1.5 \times 10^{-4}$ to be compared with a standard deviation of $1.1 \times 10^{-4}$ for the diamond data over the same range in pressure. On the other hand, a fit of this form to the MX86Ruby-scale over the same region results in $q = 5.2$ and $v_f/v_0 = 1.084$ with the much larger standard deviation of $3.2 \times 10^{-4}$. Thereby one should also notice that an exponent 5 is exactly what one expects from a point charge model for this line shift,\textsuperscript{44,45} however, $v_f/v_0 = 1.085$ or 1.084 deviates very significantly from the experimental free ion value of 1.0454 as illustrated also in Fig. 4.

On the other hand, this fitting illustrates that this smooth volume dependence fits much better to the present HP02Ruby-scale than to the MX86Ruby-scale, but on the other hand, both pressure dependent forms MX86 and HP02 result in very unreasonable variations at negative pressures, especially when the relative density decreases below 0.87, where the rupture pressure is reached. This points to the fact that no simple pressure dependent form can represent the ruby line shift over extended regions in pressure.

On the other hand, there is also no reason to trust in the simple point charge model. It therefore appears more reasonable to use a series expansion with respect to the scaled interatomic distance $x$ in the form:

$$v = v_s - v_0 x^{-5} (C_0 + C_1 x + C_2 x^2).$$  

If one constrains this series expansion to the free ion value $v_s$ and to the experimentally given slope at $x = 1$, one obtains a best fit with $C_2 = v_s/v_0 - 1 - C_1 - C_0 = -0.39$, $C_1 = 3(K_0(A - v_s/v_0 + 1)) - 2C_0 = 0.58$, and $C_0 = -0.145$, however, only with $A = 1790\,\text{GPa}$ instead of the previously used value for $A = 1820\,\text{GPa}$. This third order fit is illustrated in Fig. 4 by the dash-triple-dotted line, which obviously represents the experimental data equally well as HP02. In fact, the standard deviation between this form and HP02 in the experimental region from 0 to 150 GPa is only $0.6 \times 10^{-4}$, or in other words, much smaller than the scatter of the experimental data for diamond. Both forms of Eqs. (4) and (5) as well as HP02, but not MX86, result in the expected crossover to $v = 0$ at finite compression around $v = 0.4$, and both forms, Eqs. (4) and (5) describe the variation at negative pressures or expanded volumes more reasonably than the primarily pressure dependent forms MX86 and HP02, which produce maxims at the rupture pressure (the largest negative pressure of about --42 GPa) at a relative density of about 0.87. At lower densities the pressure dependent forms lead to a decrease down to the zero pressure value $v_0$, but not to the more reasonable approach towards the free-ion-value $v_s$. In both cases, Eqs. (4) and (5), a good fit near $x = 1$ is only obtained for $A \approx 1790\,\text{GPa}$, and this fact may be considered as another support for the HP02Ruby-scale with its smaller values for $A$. The anomalous variations of the pressure dependent forms Eqs. (1) and (2) near ambient pressure are also seen in the inset in Fig. 4, which presents an enlarged view of the small differences between the different forms with respect to the most regular first order polynomial Eq. (4) at moderate pressures. The special wiggles for the MX86 Ruby-scale can be related to the special constraints of this form and may be considered as artifacts related to the unreasonable variation at negative pressures or $\rho/\rho_0 < 1$, which is also shown in this range by the pressure dependent HP02 Ruby-scale.

CONCLUSION

As a result of the present discussion one should finally admit that

1) the slopes of the “linear” PB75Ruby-scales represent average shifts for finite ranges in pressure and not the best value for the initial slope $A$ of a nonlinear scale.

2) The rather large values for $A$ in the “nonhydrostatic” BM78Ruby-scale was obviously motivated by the specially large values for $K_0$ from the shock wave data used in this calibration in comparison with the much smaller and more accurate $K_0$ values from ultrasonic studies used here.

3) The later “quasihydrostatic” calibrations of the MX86Ruby-scale was certainly improved not only by smaller deviatoric stresses, but also by the use of more accurate values for $K_0$ and $K_0^\prime$, for instance of W, which increased the curvature parameter $B$ from 5 to 7.665. With the present value for $A = 1820(30)\,\text{GPa}$ the value of $B$ for these data would further increase to $B = 10(2)$.

4) The comparison of these $W$ data with the high pressure single crystal x-ray diffraction data for diamond\textsuperscript{11} extending up to 140 GPa with “nearly hydrostatic” conditions results in the present refinements of the parameters $A = 1820(30)\,\text{GPa}$ for the initial slope and $B = 14(3)$ for the initial curvature, when the functional form Eq. (3) is used with the additional parameter $C$. The best fit results then in $C = 7.3$, however, due to a strong correlation of $C$ with $B$ and $A$ reasonable values of $C$ may range from 5 to 10. The HP02Ruby-scale represents not only a better fit of all the experimental data but provides also the expected level crossing at a finite compression of $v = 0.4$.

5) An extension of “nearly hydrostatic” measurements with He as the pressure transmitting medium to even higher pressures than 150 GPa could certainly help to determine more precisely the additional parameter $C$.

6) Also the volume dependence of the ruby line shift has been determined already\textsuperscript{42} by combined x-ray diffraction and luminescence measurements under pressures up to 175 GPa, nonhydrostaticity with line broadening and the energy dispersive x-ray diffraction technique limited the accuracy of this study more than other more recent high-pressure studies.
Therefore a more accurate determination of the parameters in the distant dependent forms Eqs. (4) and (5) also appears to be feasible now.

(7) With the present HP02Ruby-scale the theoretical screening functions may also show a simpler form.

(8) Finally, any high pressure study using the ruby luminescence for pressure determination should now clearly state whichruby scale was used to allow for future readjustments of the data evaluations, and any evaluation of $K_0$ and $K'_0$ values from x-ray measurements using the ruby line shift for pressure determinations should not only show the standard deviations of the curve fitting procedure but should give realistic error estimates including the uncertainty of the ruby scale to allow for meaningful comparisons with ultrasonic and theoretical data. Thereby the present best estimates for $A = 1820(30)$ GPa, $B = 14(2)$, and $C = 7.3$ should be used with the given uncertainties. Especially for incompressible materials like diamond, ruby, and some of the transitions metals the change in $B$ from $7.665$ or even from $5$ in some of the earlier studies to the present value of $14$ should be taken into account, when the (systematic) errors in the values for $K'_0$ are discussed, since the standard deviations of the fits presented in most papers are typically an order of magnitude smaller than the absolute uncertainties. Thereby Eq. (2) may be very useful both for experimentalists and theoreticians to allow for a first estimate of the absolute uncertainties.

ACKNOWLEDGMENT

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11. R. LeToullec and P. Loubeye, in International Conference on High Pressure Science and Technology, Abstracts, Beijing International Convention Center, Beijing, China, 2001, p. 32, and direct communication of the data.